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(54) Title: UNSATURATED POLYESTER GEL COATS WITH ANTIFOULING PROPERTIES

(57) Abstract: This invention relates to unsaturated polyester gel coats with antifouling properties and to the use of unsaturated polyester gel coats containing antifouling agents for applications, such as marine coatings. Unsaturated polyester gel coats with antifouling properties comprise antifouling agents selected from the group consisting of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine and N-[(fluoro-dichloro-methyl)thio]-phthalimide or a mixtures thereof. Additionally the invention relates to the preparation of unsaturated polyester gel coats having antifouling properties.

Unsaturated polyester gel coats with antifouling properties

This invention relates to the preparation of unsaturated polyester gel coats containing antifouling agents and to the use of unsaturated polyester gel coats containing antifouling agents for applications, such as marine coatings. Particularly, the invention relates to the use of non-metal containing organic compounds to give antifouling properties to unsaturated polyester gel coats. Additionally the invention relates to the preparation of unsaturated polyester gel coats having antifouling properties.

Throughout history, a number of compounds have been used to prevent fouling. Biofouling on ship hulls increases friction, which reduces their speed and manoeuvrability, causing increased fuel and maintenance costs. Ship fouling is usually prevented by using antifouling paints, which function by releasing biocides to water in order to create a high concentration of these compounds close to the paint/water interface. Undesirable accumulation of microorganisms, plants, and animals on artificial surfaces is called biological fouling. Coatings applied to the artificial surfaces submerged in water like seawater, such as ship's hulls and water pipes in order to prevent biofouling, are called antifoulants. Here antifouling effect means effective protection against slime and algae attachment on surface.

Traditionally metal compounds, such as tin compounds are used as biocides and antifouling agents. Since the use of tin compounds in marine antifouling purposes will be globally banned starting from January 1, 2008, other compounds have to be used for replacing of tin.

Patent application **JP 1995-232674** describes the preparation of antifouling resin products from Preventol A3 and unsaturated polyesters. Malonic acid is used as

antifouling agent release-promoting material. These compositions are useful for the protection of deep sea pipes and cables.

Mouldings with good prevention of marine fouling are provided in patent application **JP 1995-232675**. The mouldings comprise plastics containing antifouling agents, optionally a net-type and/or a needle-type copper alloy, and the concentration of the antifouling agent is gradually increased from the surface to the inner side of mouldings. A pipe was prepared by using unsaturated polyester, glass fibres, and Sea-Nine® as antifouling agent and cured with methyl ethyl ketone peroxide and Co naphthenate.

**WO 99/01514** discloses the use of antifouling agents such as isothiazolones (Sea-Nine®), furanones, or a combination thereof with any polymer suitable for preparation by extrusion process known to the art. Suitable polymers are ethylene-vinyl acetate copolymer (EVA), high-density polyethylene (HDPE), nylon, polypropylene (PP), and sodium ionomer, copolymer of ethylene and acrylic acid, or mixtures thereof. The antifouling agents are used at a concentration of about 0.1 to 20%. These antifouling polymers are found to be suitable for marine and fresh water applications. The broad-spectrum antifouling activity was determined to be at least 100 days in a natural aqueous environment.

Gel coats are compositions which are very sensitive to external factors such as UV-light, humidity etc. and the compatibility of components in the compositions has great importance for the properties of products and their stability. Gel coats may easily lose thixotropic properties, UV-stability, water tolerance and there may appear calcing, blistering, sponging and crumbling if the starting materials in the product are not completely compatible.

In the prior art, no non-metallic agents have been disclosed, which could be used in unsaturated polyester gel coats with antifouling properties in marine applications, such as coatings. The existing prior art does not teach how to manufacture a

gel coat with good surface properties and having good antifouling properties and thus there clearly exists a need for unsaturated polyester based gel coats with antifouling properties and good surface properties.

An object of the invention is an unsaturated polyester gel coat with antifouling properties and a method for the manufacture of such unsaturated polyester gel coat.

Another object of this invention is to provide an environmentally acceptable metal-free antifouling unsaturated polyester gel coat.

Characteristic features of the unsaturated polyester gel coat with antifouling properties and of the method for the manufacture of such unsaturated polyester gel coat are stated in the claims.

It has been surprisingly found that adding of metal-free, organic antifouling agents into unsaturated polyester gel coats does not affect the application or other properties of the unsaturated polyester gel coat and biofouling is prevented or reduced on the surface of cured unsaturated polyester gel coats containing said antifouling agents. According to the invention unsaturated polyester gel coats containing metal-free synthetic organic compounds as antifouling agents are manufactured. Preferably a synthetic organic antifouling agent selected from the group consisting of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (Sea-Nine®211), cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine (Irgarol® 1051), and N-[(fluorodichloro-methyl)thio]-phthalimide (Preventol® A3) or a combination thereof is incorporated into the unsaturated polyester gel coat. Sea-Nine® is also registered with the US Environmental Protection Administration for use in marine paints and Irgarol® is approved in the USA for use in antifouling paints.

In the manufacture of an unsaturated polyester gel coat containing an antifouling agent any conventional unsaturated polyester gel coat can be used. Traditionally gel coats comprise unsaturated polyester resins based on isophthalic acid, ortophthalic acid or isophthalic acid with neopentyl glycol.

The method for the manufacture of an unsaturated polyester gel coat with antifouling properties is described in detail in the following. An unsaturated polyester gel coat, such as a standard isophthalic based white gel coat (ISO) with Brookfield viscosity of 6000-8000 mPas and styrene content of 26-30% is ground suitably in a dispergator. 0.5-10 wt-%, preferably 1-6 wt-% of an antifouling agent such as 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine or N-[(fluorodichloromethyl)-thio]-phthalimide or a mixture thereof, is ground or dissolved into the gel coat. The grinding is continued until a well-dispersed solution with a particle size of 60 μm or less is achieved. The viscosity and thixotropy index of the obtained product are suitable for applications of unsaturated polyester gel coats. The viscosity differs not more than ± 2000 mPas from the original viscosity of the unsaturated polyester gel coat and the thixotropy index differs not more than ± 1.5 from the original thixotropy index. Typically for spraying quality the Brookfield viscosity of the product is 4000-8000 mPas and the thixotropy index is 3.5-5.5.

Unsaturated polyester gel coats according to the invention may also be manufactured using Master Batch method without effecting on the gel coat properties, such as curing properties. The Master Batch method consists of 4 stages wherein thixotropic master, filler master and pigment master are prepared separately and then they are mixed together with additives and solvent.

Unsaturated polyester gel coats are curable compositions, which contain unsaturated polyester resins with additives. Suitable additives include thixotropic agents, thixotropy enhancers, suppressants, surface tension agents, co-promoters, promoters, air releasing agents, fillers, wetting agents, levelling agents and pigments.

The thixotropic agents comprise silica compounds, such as fumed silica and precipitated silica and inorganic clays like bentonite and hectorite clay.

Thixotropy enhancers comprise propylene glycol and ethylene glycol and derivatives thereof.

Promoters are usually added to unsaturated polyester resins to accelerate the decomposition of a peroxide initiator into free radicals and to thereby initiate or speed up the curing of the composition. The promoters are generally metal compounds, such as cobalt, maganese, iron, vanadium, and aluminium salts of organic acids, such as octoate of naphthenate salts.

Co-promoters are widely used in promoter systems and suitable ones are organic amines like dimethylaniline, diethylaniline, 2-aminopyridine, N,N-dimethylacetoacetamide, acetoacetanilide or other organic compounds like ethyl acetoacetate, methyl acetoacetate and N,N-dimethyl-p-toluidine.

Inhibitors are used for adjusting storage stability and gel time, and suitable inhibitors comprise hydroquinone, toluhydroquinone, mono-tert-butylhydroquinone, hydroquinone monomethyl ether p-benzoquinone, 2,5-di-tert-butylhydroquinone.

Unsaturated polyester gel coats may also contain fillers such as talc, calcium carbonate, magnesium carbonate, barium carbonate, aluminium trihydroxide, calcium sulfate, magnesium sulfate, barium sulfate, chopped glassfiber and the like.

Various pigments are typically used in gel coats and titanium dioxide is a suitable one.

Air release agents, wetting additives, surfactants or levelling additives based on silicone and fluorocarbons and various modified polymers like acrylate and urethane may be added to gel coats.

Suppressants for reducing organic emissions may be included in gel coats and polyethers, alcanoic acid esters of propoxylated phenols, propoxylated bisphenols or hydroxypropylphthalates, polyetherpolysiloxane blockcopolymers, waxes and the like are suitable suppressants.

Various peroxides for curing/crosslinking are used and peroxides like methyl ethyl ketone peroxide, cumene hydroperoxide, t-butyl peroctoate, di-t-butyl peroxide, benzoyl peroxide and the like are suitable.

The unsaturated polyester gel coats with antifouling properties according to the invention are well suited for hand lay up lamination, spray lamination, resin lamination, pultrusion, sheet moulding compounding, bulk moulding compounding and applications well known to the man skilled in the art.

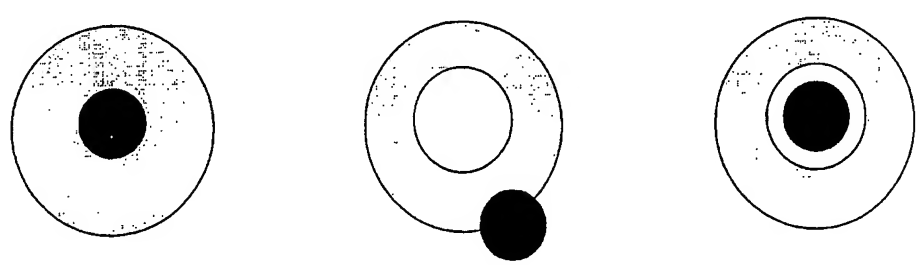
Especially the unsaturated polyester gel coats with antifouling properties according to the invention are suitable for marine applications and for surfaces needing protection against biofouling.

The unsaturated polyester gel coats with antifouling properties according to the invention have been tested as marine coatings. Application properties are similar to standard gel coats and the workability of gel coats is retained for an appropriate period. Surprisingly it was noticed that when compared the unsaturated polyester gel coats containing antifouling agents to conventional unsaturated polyester gel coats, the coating maintains its surface performance, which was demonstrated by running weather stability test (QUV) and blistering test.

The antifouling effect was determined by immersing test panels in water containing alga population for 7 weeks exposure. The edges of the panels were coated with top coat without any biocides. When companing the attachment of algae to the unsaturated polyester gel coats containing antifouling agents and to the top coat, the top coat was found to be significantly more fouled than the gel coat containing biocides. The unsaturated polyester gel coats containing antifouling agents prevents or reduces fouling significantly.

The ability of the unsaturated polyester gel coats according to the invention to prevent the growth of algae on the surface was determined using algae growth inhibition test. Unsaturated polyester gel coat samples containing antifouling agents inhibit the growth of algae and some combinations even prevent the growth totally. The test method is described in the following: Agar plates with growing cultures of unicellular green algae are incubated for 7 days under standardized conditions. Unsaturated polyester gel coat samples containing antifouling agents are placed on the surface of the agar. The antifouling effect is determined qualitatively by visual assessment of the growth of the algae.

The samples are assessed using Vinson rating-method. (Vinson rating: L.J. Vinson et al. J. Pharm. Sci. 50 (1961), 827-830.) After incubation the inhibition zone (=growth-free zone around the disc) is measured and given in millimetres (see illustration). If there is no inhibition zone, the disc must be removed and the disc is checked with a microscope.



| Inhibition zone, mm | Growth beneath the disc | Vinson Rating | Assessment zones |
|---|---|---|---|
| 0 | Yes | 0 | No activity |
| 0 | Isolated colonies | 1 | Slight activity |
| 0 | Isolated colonies or very small colonies | 2 | Fair activity |
| 0 | No | 3 | Good activity |
| 1-n | No | 4 | Very good activity |

The unsaturated polyester gel coat with antifouling agents has good applicability and retains its' viscosity and stability, and as a cured product it has excellent UV- and weathering stability and yields good final surface.

The invention is illustrated in more detail in the following examples, to which however the scope of the invention is not limited.

**Example 1.** Manufacturing of an unsaturated polyester gel coat containing Irgarol®

A standard isophthalic based (ISO) white gel coat with Brookfield viscosity of 4000 mPas (20 rpm, spindle 4), thixotropy index of 5.3, I.C.I of 2.1 P and styrene content of 26-30% or a low styrene ISO NPG gel coat (white) with Brookfield viscosity of 3800 mPas (20 rpm, spindle 4), thixotropy index of 4, I.C.I of 4.1 P and styrene content of 26-30% was ground in a dispergator (1500 rpm). 1, 2, and 3 wt-% of Irgarol® was ground into the gelcoat. The grinding was continued for 10 minutes. When adding of 3 wt-% of Irgarol® the achieved Brookfield viscosity (20 rpm) was 3260 mPas, thixotropy index 5.1, and I.C.I 2.4 P. The gel time of a standard white gel coat (ISO) was 6.5 minutes and the gel time of the standard white gel coat (ISO) containing 3 wt-% of Irgarol® was 6 minutes.

**Example 2.** Manufacturing of an unsaturated polyester gel coat containing Sea-Nine®

A standard isophthalic based (ISO) white gel coat with Brookfield viscosity of 4000 mPas (20 rpm, spindle 4), thixotropy index of 5.3, I.C.I of 2.1 P and styrene content of 26-30% or a low styrene ISO NPG gel coat (white) with Brookfield viscosity of 3800 mPas (20 rpm, spindle 4), thixotropy index of 4, I.C.I of 4.1 P and styrene content pf 26-30% was ground in a dispergator (1500 rpm). 1, 2, and 3 wt-% of Sea-Nine® was ground into the gelcoat. The grinding was continued for 10 minutes. When adding of 1 wt-% of Sea-Nine® the achieved Brookfield viscosity (20 rpm) was 3470 mPas, thixotropy index 5.2, and I.C.I 2.3 P. The gel time of a standard white gel coat (ISO) was 6.5 minutes and the gel time of the standard white gel coat (ISO) containing 1 wt-% of Sea-Nine® was 6 minutes.

**Example 3.** Manufacturing of an unsaturated polyester gel coat containing Preventol®

A standard isophthalic based (ISO) white gel coat with Brookfield viscosity of 4000 mPas (20 rpm, spindle 4), thixotropy index of 5.3, I.C.I of 2.1 P and styrene content of 26-30% or a low styrene ISO NPG gel coat (white) with Brookfield viscosity of 3800 mPas (20 rpm, spindle 4), thixotropy index of 4, I.C.I of 4.1 P and styrene content of 26-30% was ground in a dispergator (1500 rpm). 1, 2, and 3 wt-% of Preventol® was ground into the gelcoat. The grinding was continued for 10 minutes. When adding of 3 wt-% of Preventol® the achieved Brookfield viscosity (20 rpm) was 3730 mPas, thixotropy index 5.2, and I.C.I 2.1 P. The gel time of a standard white gel coat (ISO) was 6.5 minutes and the gel time of the standard white gel coat (ISO) containing 3 wt-% of Preventol® was 7 minutes.

**Example 4.** Application of unsaturated polyester gel coats having antifouling properties

The coatings manufactured from the unsaturated polyester gel coats containing antifouling agents from Examples 1-3 maintain surface performance, which was determined by weather stability test (QUV) and blistering test. The properties of the coatings are presented in Tables I-IV.

Table I The results of weather stability test (QUV) and blistering test when using Irgarol®.

| Coating | DE (C-Lab) (after 1000 h exposure in weather test) | Blistering (samples exposed to 65°c water for 21 days) |
|---|---|---|
| STD white gel coat (reference) | 5.63 | NO BLISTERS |
| STD white gel coat + Irgarol 1% | 6.75 | NO BLISTERS |
| STD white gel coat + Irgarol 2% | 4.75 | NO BLISTERS |
| STD white gel coat + Irgarol 3% | 4.86 | NO BLISTERS |

Table II The results of weather stability test (QUV) and blistering test when using Irgarol®.

| Coating | dE (C-Lab) (after 1000 h exposure in weather test) | Blistering (samples exposed to 65°c water for 21 days) |
|---|---|---|
| Low styrene ISO NPG gel coat (reference) | 4.42 | NO BLISTERS |
| Low styrene ISO NPG gel coat + Irgarol 1% | 4.02 | NO BLISTERS |
| Low styrene ISO NPG gel coat + Irgarol 2% | 4.05 | NO BLISTERS |
| Low styrene ISO NPG gel coat + Irgarol 3% | 3.69 | NO BLISTERS |

Table III The results of weather stability test (QUV) and blistering test when using Sea-Nine®.

| Coating | dE (C-Lab) (after 1000 h exposure in weather test) | Blistering (samples exposed to 65°c water for 21 days) |
|---|---|---|
| STD white gel coat (reference) | 5.63 | NO BLISTERS |
| STD white gel coat + Sea-Nine 1% | 6.79 | NO BLISTERS |
| STD white gel coat + Sea-Nine 2% | 8.6 | NO BLISTERS |
| STD white gel coat + Sea-Nine 3% | 8.86 | NO BLISTERS |

Table IV The results of weather stability test (QUV) and blistering test when using Preventol.

| Coating | dE (C-Lab) (after 1000 h exposure in weather test) | Blistering (samples exposed to 65°c water for 21 days) |
|---|---|---|
| Low styrene ISO NPG gel coat (reference) | 4.42 | NO BLISTERS |
| Low styrene ISO NPG gel coat + Preventol 1% | 5.84 | NO BLISTERS |
| Low styrene ISO NPG gel coat + Preventol 2% | 6 | FEW SMALL BLISTERS |

**Example 5.** Application of an unsaturated polyester gel coat with antifouling properties

The compatibility of antifouling agents with unsaturated polyester gel coats was determined by measuring Brookfield viscosity. The stability of Brookfield viscosity after 3 months storage was even found to improve when combining unsaturated polyester gel coats with antifouling agents. The results are presented in Tables V-VII.

Table V Brookfield viscosity and the stability when using Irgarol® as an antifouling agent.

| | BROOKFIELD VISCOSITY [mPas] | I.C.I, [P] | T.I. | BROOKFIELD VISCOSITY (3 MONTHS) [mPas] | I.C.I, [P] | T.I. |
|---|---|---|---|---|---|---|
| STD white gel coat (reference) | 4060 | 2.1 | 5.3 | 3600 | 2 | 5.1 |
| Low styrene ISO NPG gel coat (white) | 3800 | 4.1 | 4 | 3230 | 4.5 | 3.6 |
| STD gel coat + Irgarol 1% | 3880 | 2.2 | 5.4 | 3630 | 2.4 | 5.1 |
| STD gel coat + Irgarol 2% | 3520 | 2.2 | 5.2 | 3380 | 2.6 | 5 |
| STD gel coat + Irgarol 3% | 3260 | 2.4 | 5.1 | 3200 | 2.4 | 5 |
| Low styrene ISO NPG gel coat + Irgarol 1% | 3820 | 4.2 | 4.2 | 3380 | 4.4 | 3.8 |
| Low styrene ISO NPG gel coat + Irgarol 2% | 3750 | 4.4 | 4.1 | 3460 | 4.5 | 3.7 |
| Low styrene ISO NPG gel coat + Irgarol 3% | 3740 | 4.6 | 4 | 3450 | 4.6 | 3.6 |

Table VI Brookfield viscosity and the stability when using Sea-Nine® as an antifouling agent.

| | BROOKFIELD VISCOSITY [mPas] | I.C.I, [P] | T.I. | BROOKFIELD VISCOSITY (3 MONTHS) [mPas] | I.C.I, [P] | T.I. |
|---|---|---|---|---|---|---|
| STD white gel coat (reference) | 4060 | 2.1 | 5.3 | 3600 | 2 | 5.1 |
| Low styrene ISO NPG gel coat (white) | 3800 | 4.1 | 4 | 3230 | 4.5 | 3.6 |
| STD gel coat + Sea-Nine 1% | 3470 | 2.3 | 5.2 | 3310 | 1.9 | 5.1 |
| STD gel coat + Sea-Nine 2% | 3110 | 1.8 | 5.2 | 2970 | 1.8 | 5.1 |
| Low styrene ISO NPG gel coat + Sea-Nine 1% | 3170 | 3.6 | 4 | 2950 | 3.6 | 3.7 |
| Low styrene ISO NPG gel coat + Sea-Nine 2% | 2710 | 3 | 4 | 2500 | 3.4 | 3.7 |

Table VII Brookfield viscosity and the stability when using Preventol® as an antifouling agent.

| | BROOKFIELD VISCOSITY [mPas] | I.C.I, [P] | T.I. | BROOKFIELD VISCOSITY (3 MONTHS) [mPas] | I.C.I, [P] | T.I. |
|---|---|---|---|---|---|---|
| STD white gel coat (reference) | 4060 | 2.1 | 5.3 | 3600 | 2 | 5.1 |
| Low styrene ISO NPG gel coat (white) | 3800 | 4.1 | 4 | 3230 | 4.6 | 3.6 |
| STD gel coat + Preventol 1% | 4040 | 2.4 | 5.2 | 3820 | 2.2 | 5.1 |
| STD gel coat + Preventol 2% | 3800 | 2.2 | 5.2 | 3730 | 2.3 | 5.1 |
| STD gel coat + Preventol 3% | 3730 | 2.1 | 5.2 | 3520 | 2.2 | 5.1 |
| Low styrene ISO NPG gel coat + Preventol 1% | 4040 | 4 | 4 | 3410 | 4.2 | 3.7 |
| Low styrene ISO NPG gel coat + Preventol 2% | 3640 | 4.2 | 3.9 | 3390 | 4.6 | 3.7 |
| Low styrene ISO NPG gel coat + Preventol 3% | 3640 | 4.2 | 3.9 | 3400 | 4.2 | 3.6 |

**Example 6.** Application of an unsaturated polyester gel coat having antifouling properties

The compatibility of antifouling agents with unsaturated polyester gel coats was determined by monitoring curing properties. Gel time (GT), peak exotherm (PET) and curing time (GTP) are presented in Table VIII.

From the test results it can be seen that dispersing of an antifouling agent in gel coat does not have an effect on gel time or its stability after 3 months. Different antifouling agents have different effects on peak exotherm (PET) and on the curing time (GTP).

Table VIII. Curing properties of unsaturated polyester gel coat containing 3 wt-% of active ingredients.

| | GT, MIN | GT, MIN (2-3 MONTHS) | PET, °C | PET, °C (2-3 MONTHS) | GTP, MIN | GTP, MIN (2-3 MONTHS) |
|---|---|---|---|---|---|---|
| STD white STD gel coatl coat | 6.5 | 6 | 145 | 137 | 23.5 | 27.5 |
| Low styrene ISO NPG STD gel coat | 6 | 8.5 | 137 | 139 | 11 | 11.5 |
| STD GEL COAT + IRGAROL 3% | 6 | 6 | 137 | 137 | 17.5 | 19 |
| Low styrene ISO NPG STD gel coat + IRGAROL 3% | 7 | 7.5 | 137 | 135 | 7.5 | 8 |
| STD GEL COAT + SEA-NINE3% | 7 | 7 | 92 | 76 | 40 | 45 |
| Low styrene ISO NPG STD gel coat + SEA-NINE3% | 8.5 | 10 | 111 | 109 | 16 | 17.5 |
| STD GEL COAT + PREVENTOL3% | 7 | 5.5 | 121 | 104 | 30 | 35.5 |
| Low styrene ISO NPG STD gel coat + PREVENTOL3% | 7 | 7 | 125 | 125 | 13 | 14 |

**Example 7.** Application of unsaturated polyester gel coats having antifouling properties

The attachment of algae to the unsaturated polyester gel coats comprising antifouling agents and to top coat without antifouling agents was monitored. The top coat was found to be more fouled than the gel coat containing antifouling agents. Pictures of test panels, after 7 weeks exposure in water containing alga population, are presented in Figure 1 and Figure 2.

**Example 8.** Application of unsaturated polyester gel coats having antifouling properties

The application of the unsaturated polyester gel coat having antifouling properties can be applied in any of the above mentioned ways and in the following a description of the manufacture of laminates is provided. The prepared unsaturated

polyester gel coat was initiated with 2 % of methyl ethyl ketone peroxide and applied to the surface with an applicator making film thickness of 200-2000 μm, preferably, 300-1000 μm (wet thickness). After the gelation, the background was laminated with standard orto-phthalic polyester resin and with 4 layers of glass fiber mats. The gel laminate was post cured in the oven at 50°C for 5 hours and at 80°C for 3 hours. Test pieces were sawed from the post-cured laminate.

The surface of an unsaturated polyester gel coat was observed by using Scanning Electron Microscope (SEM). After 3 weeks exposure in 65°C water no 'sponge-effect' was seen on the surface. Water has not dissolved the antifouling agents out of the coating.

**Examples 9 - 16.** Manufacturing of a gel coat having antifouling properties

A low styrene ISO NPG gel coat (white) with Brookfield viscosity of 3800 (20 rpm, spindle 4), thixotropy index of 4, I.C.I of 4.1 P and styrene content of 26-30% was ground in a dispergator (1500 rpm). Different combinations of Irgarol®, Sea-Nine® and Preventol® were ground into the gelcoat. The grinding was continued 10 minutes. Combinations and the properties of the gel coats containing biocides are presented in Tables IX and X.

Table IX Combinations and the properties of the gel coats containing biocides.

| GEL COATS | | | | |
|---|---|---|---|---|
| Constituent (weight-%) | Example 9 | Example 10 | Example 11 | Example 12 |
| Resin | 53 | 53.5 | 53.5 | 54.5 |
| Styrene | 13.7 | 13.35 | 13.35 | 12.75 |
| Air release agent | 0.2 | 0.2 | 0.2 | 0.2 |
| Fillers | 13.9 | 14.1 | 14.1 | 14.2 |
| Titanium dioxide | 13.8 | 14 | 14 | 14.2 |
| Thixotropic agent | 1.2 | 1.2 | 1.2 | 1.2 |
| Promoters | 0.45 | 0.45 | 0.45 | 0.45 |
| Inhibitor | 0.2 | 0.2 | 0.2 | 0.2 |
| | | | | |
| Irgarol® 1051 | 2.5 | 2 | 1 | |
| Sea-Nine® 211 | 0.55 | 1 | 2 | 2 |
| Preventol® A3 | 0.5 | | | 0.3 |
| **Property:** | | | | |
| Brookfield viscosity/ 20 RPM | 1810 | 2010 | 2070 | 2320 |
| Thixotropic index 5/50 RPM | 4 | 4.1 | 4.1 | 4.2 |
| I.C.I | 2.2 | 3.6 | 2.6 | 2.6 |
| Gel time, min | 12.5 | 13.5 | 12.5 | 13 |

Table X Combinations and the properties of the gel coats containing biocides.

| GEL COATS | | | | |
|---|---|---|---|---|
| Constituent (weight-%) | Example 13 | Example 14 | Example 15 | Example 16 |
| Resin | 50 | 50 | 50 | 54.7 |
| Styrene | 15.6 | 15.6 | 15.6 | 12.5 |
| Air release agent | 0.2 | 0.2 | 0.2 | 0.2 |
| Fillers | 13.2 | 13.2 | 13.2 | 14.4 |
| Titanium dioxide | 13.2 | 13.2 | 13.2 | 14.3 |
| Thixotropic agent | 1.2 | 1.2 | 1.2 | 1.2 |
| Promoters | 0.4 | 0.4 | 0.4 | 0.5 |
| Inhibitor | 0.2 | 0.2 | 0.2 | 0.2 |
| | | | | |
| Irgarol® 1051 | 4 | 4 | 6 | |
| Sea-Nine® 211 | 2 | | | 2 |
| Preventol® A3 | | 2 | | |
| **Property:** | | | | |
| Brookfield viscosity/ 20 RPM | 1540 | 1590 | 820 | 2970 |
| Thixotropic index 5/50 RPM | 4.2 | 4.3 | 4 | 4.6 |
| I.C.I | 1.7 | 1.7 | 1 | 2.7 |
| Gel time, min | 17.5 | 14.5 | 19 | 15 |

**Example 17.** Application of unsaturated polyester gel coats having antifouling properties

The compatibility of different combinations of antifouling agents with unsaturated polyester gel coats was determined using weather stability test (QUV). The coatings were found to maintain good weather stability properties and some of the combinations even improved the stability. The results are presented in Table XI.

Table XI The results of weather stability test (QUV) when using different combinations of biocides.

| Coating | dE (C-lab) (after 1000 h of exposure in weather test) |
|---|---|
| Reference | 4.42 |
| Example 9 | 3.39 |
| Example 10 | 3.03 |
| Example 11 | 4.04 |
| Example 12 | 4.87 |
| Example 13 | 3.51 |
| Example 14 | 3.9 |
| Example 15 | 2.84 |
| Example 16 | 4.56 |

**Example 18.** Application of unsaturated polyester gel coats having antifouling properties

The attachment of algae to the unsaturated polyester gel coats comprising antifouling agents was monitored by algae growth inhibition test. The test method is described on page 7. The gel coat samples containing antifouling agents were found effective against algae growth. Some combinations prevented algae growth

totally. The results are presented in the Table XII. Pictures of gel coat samples after 7 days of exposure are presented in Figure 3, Figure 4, Figure 5, Figure 6 and Figure 7.

Table XII Some results of algae growth inhibition test.

| COATING | VINSON RATING | ALGAE GROWTH INHIBITION |
|---|---|---|
| Reference | 0 | No activity |
| Example 9 | 3 | Good activity |
| Example 10 | 3 | Good activity |
| Example 13 | 4 | Excellent activity |
| Example 14 | 4 | Excellent activity |
| Example 15 | 3 | Good activity |
| Example 16 | 3 | Good activity |

Claims

1. Unsaturated polyester gel coat with antifouling properties, **characterised** in that the unsaturated polyester gel coat comprises an antifouling agent selected from the group consisting of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, cyclo-propyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine and N-[(fluorodichloro-methyl)thio]-phthalimide or a mixture thereof.

2. Unsaturated polyester gel coat with antifouling properties according to claim 1, **characterised** in that the amount of the antifouling agent is 0.5-10 wt-%.

3. Unsaturated polyester gel coat with antifouling properties according to claim 1 or 2, **characterised** in that the amount of the antifouling agent is 1-6 wt-%.

4. Unsaturated polyester gel coat with antifouling properties according to any one of claims 1-3, **characterised** in that the unsaturated polyester gel coat is based on isophthalic acid, ortophthalic acid or isophthalic acid with neopentyl glycol.

5. Unsaturated polyester gel coat with antifouling properties according to any one of claims 1-4, **characterised** in that it comprises additionally thixotropic agents, thixotropic enhancers, suppressants, surface tension agents, copromotors, promotors, air releasing agents, fillers, wetting agents, levelling agents and pigments.

6. Use of the unsaturated polyester gel coats with antifouling properties according to any one of claims 1-5, **characterized** in that said gel coats are used in hand lay up lamination, spray lamination, resin lamination, pultrusion, sheet moulding compounding and bulk moulding compounding.

7. Use of the unsaturated polyester gel coats with antifouling properties according to any one of claims 1-5, **characterized** in that said gel coats are used in marine applications and for surfaces requiring protection against biofouling.

8. Method for the manufacture of unsaturated polyester gel coats with antifouling properties, **characterized** in that an unsaturated polyester gel coat is ground and 0,5-10 wt-% of an antifouling agent selected from a group consisting of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, cyclopropyl-N'-(1,1-dimethyl-ethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine and N-[(fluorodichloro-methyl)-thio]-phthalimide or a mixture thereof is ground or dissolved in the gel coat, and the grinding is continued until a well dispersed solution is achieved.

9. Method according to claim 8, **characterized** in that 1-6 wt-% of an antifouling agent or a mixture thereof is used.

10. Method according to claim 8 or 9, **characterized** in that the unsaturated polyester gel coat is based on isophthalic acid, ortophthalic acid or isophthalic acid with neopentyl glycol and that additionally compounds selected from the group consisting of thixotropic agents, thixotropic enhancers, suppressants, surface tension agents, copromotors, promotors, air releasing agents, fillers, wetting agents, levelling agents and pigments are ground to the gel coat.

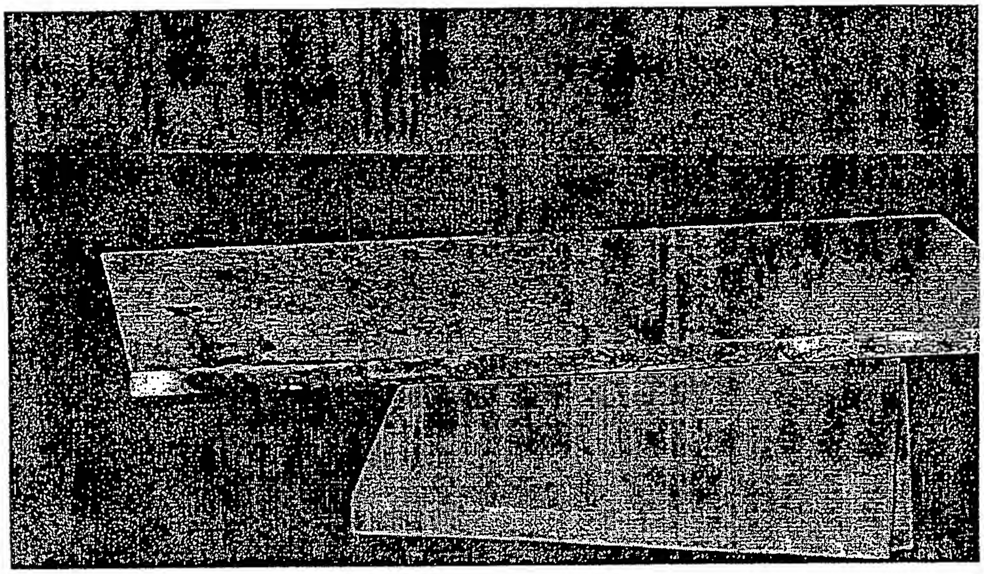


Figure 1. Unsaturated polyester gel coat containing 3 wt-% of Sea-Nine® after 7 weeks exposure in water containing alga population.

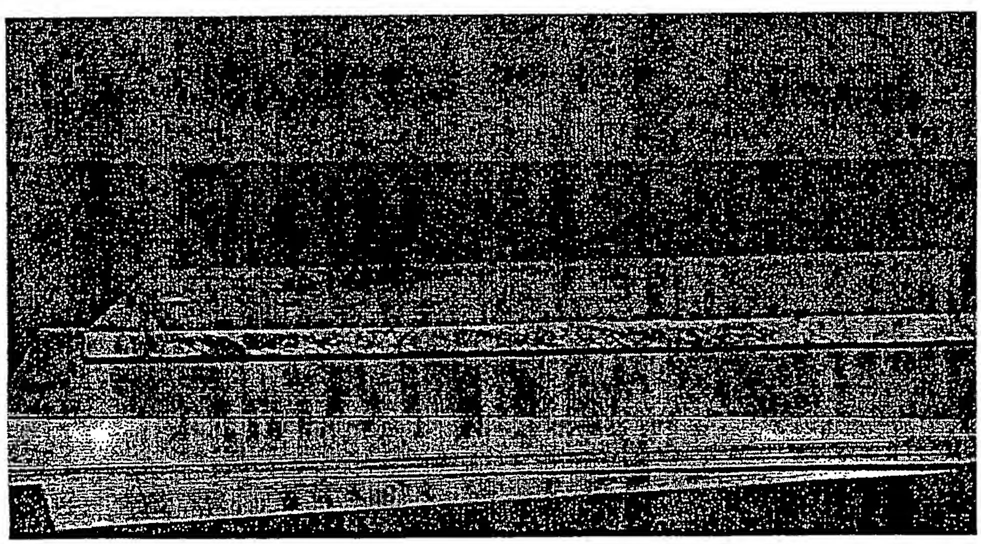


Figure 2. Unsaturated polyester gel coat containing 3 wt-% of Irgarol® after 7 weeks exposure in water containing alga population.


Figure 3 Unsaturated polyester gel coat containing gel coat according to Example 13.


Figure 4. Unsaturated polyester gel coat containing gel coat according to Example 14.

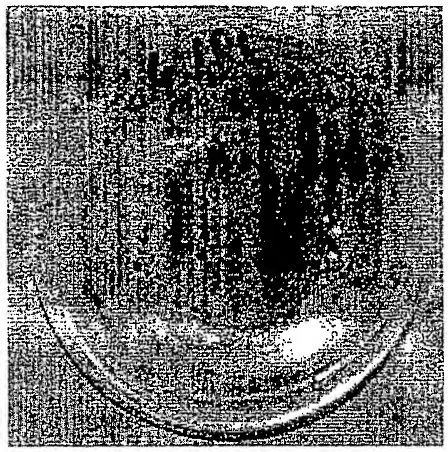


Figure 5. Unsaturated polyester gel coat according to Example15.

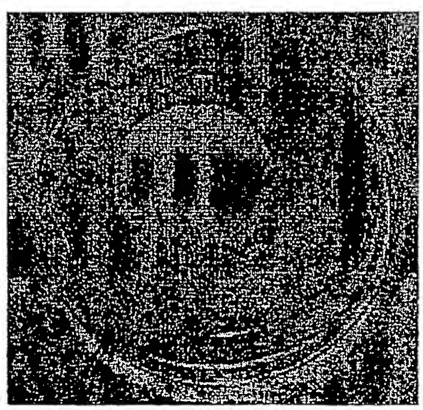


Figure 6. Unsaturated polyester gel coat containing no biocides (reference)

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 01/00195

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7: C09D 5/16, C08K 5/34, C09D 5/36
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C09D, C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| P,X | EP 1057856 A1 (CIBA SPECIALTY CHEMICALS HOLDING INC.), 6 December 2000 (06.12.00), page 2, line 3 - line 36; page 4, line 55 - page 5, line 4; page 12, line 44 - line 55, abstract<br>-- | 1-11 |
| A | WPI/Derwent's abstract, Accession Number 1996-408281 week 9641, ABSTRACT OF JP, 8198720 (SEKISUI CHEM IND CO LTD) 06 August 1996 (06.08.1996)<br>-- | 1-10 |
| A | Patent Abstracts of Japan, Vol 199,No 12 abstract of JP 81-98720 A (SEKISUI CHEM CO LTD), 6 August 1996 (06.08.96)<br>-- | 1-10 |

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 9 July 2001 | 19 -07- 2001 |



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 01/00195

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | WPI/Derwent's abstract, Accession Number 1997-337015, week 9731, ABSTRACT OF JP, 9136803 (SEKISUI CHEM IND CO LTD) 27 May 1997 (27.05.1997) -- | 1-11 |
| A | Patent Abstracts of Japan, Vol 199,No 709 abstract of JP 91-36803 A (SEKISUI CHEM CO LTD), 27 May 1997 (27.05.97) -- | 1-11 |
| A | WPI/Derwent's abstract, Accession Number 1997-521824, week 9748, ABSTRACT OF JP, 9249507, (TAISEI CONSTR CO LTD) 22 September 1997 (22.09.1997) -- | 1-11 |
| A | Patent Abstracts of Japan, Vol 199,No 801 abstract of JP 92-49507 A (TAISEI CORP), 22 Sept 1997 (22.09.97) -- | 1-11 |
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**INTERNATIONAL SEARCH REPORT**
Information on patent family members

International application No.
PCT/FI 01/00195

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | JP 2001002930 A | 09/01/01 |
| GB 2277742 A | 09/11/94 | GB 9407915 D | 00/00/00 |
| | | JP 6305913 A | 01/11/94 |

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